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Origin of the enhanced performance in poly(3-hexylthiophene): [6,6]-phenyl C₆₁-butyric acid methyl ester solar cells upon slow drying of the active layer

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The origin of the enhanced performance of bulk heterojunction solar cells based on slowly dried films of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C₆₁-butyric acid methyl ester is investigated, combining charge transport measurements with numerical device simulations. Slow drying leads to a 33-fold enhancement of the hole mobility up to $5.0 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the P3HT phase of the blend, thereby balancing the transport of electrons and holes in the blend. The resulting reduction of space-charge accumulation enables the use of thick films ($\sim 300 \text{ nm}$), absorbing most of the incoming photons, without losses in the fill factor and short-circuit current of the device.
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Solar cells based on a blend of conjugated polymers and functionalized fullerenes are an attractive option for cost effective, large area, and light-weight applications.¹ Initially, the attention has mainly been focused on blends of poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylene vinylene) (MDMO-PPV) and [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM). By optimizing the morphology of the MDMO-PPV:PCBM BHJ, certified AM1.5 power efficiencies of 2.5% (with [60]PCBM) and 3% (with [70]PCBM) have been achieved.^{2–4} Recently, we have developed a device model that quantitatively describes the operation characteristics of PPV:PCBM BHJ solar cells.⁵ An important process that limits the photocurrent is the dissociation of bound electron-hole pairs, formed after the ultrafast electron transfer at the donor/acceptor interface.⁶ Another remarkable feature of MDMO-PPV:PCBM solar cells is that the optimum performance is reached adding up to 80 wt % of PCBM, a hardly absorbing material in the solar spectral region.³ The necessity of such a large amount of PCBM arises from a strong enhancement of the hole transport in MDMO-PPV when blended with PCBM,⁷ combined with an enhanced dissociation efficiency due to the increase of the dielectric constant.⁸ For PPV-based compounds with lower hole mobilities we have demonstrated that the photocurrent reaches a fundamental space-charge limit, which is detrimental for the fill factor and efficiency.⁹

In the last 2–3 years attention has shifted from PPV-based devices towards BHJ solar cells based on regioregular poly(3-hexylthiophene) (P3HT). It has been demonstrated that thermal annealing of P3HT:PCBM blend devices strongly improves the energy conversion efficiencies up to 3.5%.¹⁰ This strong increase of the efficiency has been attributed to an increase of the hole transport due to crystallization of the polymer, a better morphology, and an improved overlap with the solar spectrum due to a redshift of the absorption

upon annealing.^{11–14} Another important breakthrough was recently realized by Li *et al.*, who demonstrated that the efficiency can exceed 4% by controlling the growth rate of the active layer.¹⁵ Slowing down the drying process of the wet films leads to an enhanced self-organization, which is expected to enhance the hole transport in the P3HT. In another study even efficiencies approaching 5% have been demonstrated, although the devices were not measured under standard AM1.5 test condition.¹⁶ The charge transport in the slowly dried P3HT:PCBM blends has been investigated using time-of-flight (TOF) measurements. Electron and hole mobilities of $\mu_e = 7.7 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\mu_h = 5.1 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ were reported, respectively.¹⁵ It should be noted that these values were not measured in highly efficient solar cell devices but in films with a thickness of $\sim 1 \mu\text{m}$, since for TOF experiments the sample should be significantly thicker than the light-absorption region. It is, however, remarkable that the reported mobility values for these slowly dried films with superior photovoltaic performance are much lower than the values reported for MDMO-PPV:PCBM and annealed P3HT:PCBM devices: For MDMO-PPV:PCBM (1:4 wt %) values of $\mu_e = 2.0 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\mu_h = 1.4 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ have been found,⁸ and for P3HT:PCBM (1:1 wt %) using fast drying and annealing similar values of $\mu_e = 3.0 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\mu_h = 1.5 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ have been measured.¹⁴ Therefore, from the reported values it is not clear whether an enhanced hole transport is responsible for the improved performance after slow drying. In the present study we perform mobility measurements in solar cells using space-charge limited (SCL) currents. It is observed that after slow drying the hole mobility of the P3HT improves to a record value of $\mu_h = 5.0 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is 33 times higher than in blends that are annealed after spin coating¹⁴ and two orders of magnitude higher than earlier reported values.¹⁵ Device simulations show that because of this increased hole transport the active P3HT:PCBM layer can be made much thicker, up to

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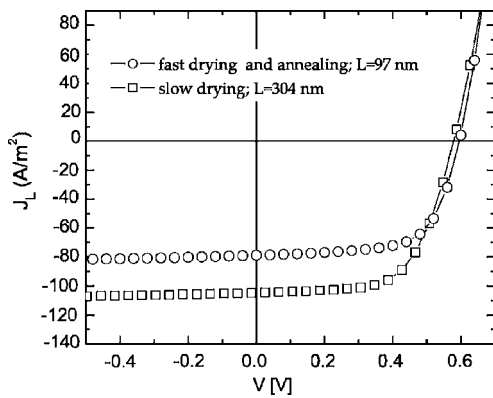


FIG. 1. Experimental photocurrent (J_L) vs applied voltage (V) of the ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al devices fabricated by two different recipes: (○) the active layer was spun from a chloroform solution, followed by thermal annealing of the completed device at 110 °C for 4 min; (□) the active layer was spun from an ODCB solution and subsequently dried in a covered Petri dish overnight before the actual top electrode was thermally deposited. The film thicknesses are also indicated.

300 nm, without a large reduction of the fill factor. The increased layer thickness then leads to an enhancement of the optical absorption, that subsequently increases the short-circuit current. Combined with the preservation of fill factor and open-circuit voltage, this leads to the observed enhancement of the power efficiency.

All devices during the course of this study were fabricated using indium tin oxide (ITO) coated glass substrates. Subsequently, an aqueous suspension of poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate) (PEDOT:PSS) (Bayer AG) was spin coated on top of the ITO surface, under ambient conditions, before drying the substrates at 140 °C in an oven. For fast drying films the active layer was fabricated by spin coating a solution of regioregular P3HT and PCBM (1:1 w/w) in chloroform on top of the PEDOT:PSS coated substrate. The devices were subsequently annealed in the nitrogen glove box on a hot plate at a temperature of 110 °C for 4 min. For slow drying films the P3HT:PCBM layer was spun from an *ortho*-dichlorobenzene (ODCB) solution on the ITO/PEDOT:PSS substrate, followed by drying of the films at room temperature in a closed Petri dish overnight.¹⁵ Subsequently, a LiF/Al top electrode was thermally evaporated to complete the devices. The hole-only devices, used to investigate hole transport in P3HT:PCBM blends, were fabricated following the same procedure presented above except for the top electrode which was replaced with palladium (Pd) (40–50 nm). In order to measure the photocurrent, the devices were illuminated by a white light halogen lamp under a dry nitrogen atmosphere. The intensity of the halogen lamp was calibrated using a Si diode to give 100 mW/cm² (without a standard compensation for the spectral mismatch).

As a first step we compare the photocurrent of solar cells prepared with either fast drying and subsequent annealing or the slow drying procedure, as shown on Fig. 1. The devices of the first type reach their optimum performance at a layer thickness L of ~ 100 nm. With a short-circuit current density $J_{sc}=79$ A/m², an open-circuit voltage $V_{oc}=0.6$ V, and a fill factor $FF=66\%$ the efficiency of these devices amounts to 3.1%. For the slowly dried films, however, the optimum performance is obtained at considerably thicker films with thicknesses of typically $L\sim 300$ nm. In these devices values

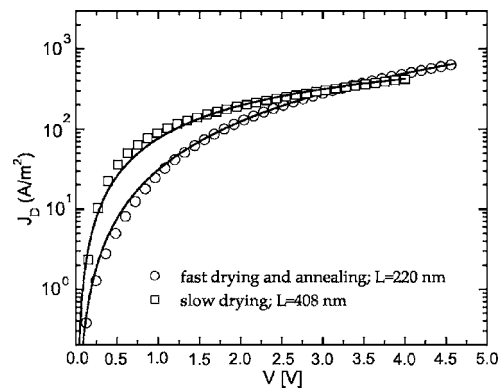


FIG. 2. Experimental dark current densities (J_D) of the 50:50 wt % P3HT:PCBM blend devices, measured at room temperature in the hole-only device configuration. The symbols correspond to different drying conditions of the photoactive layer (see text). The solid lines represent the fit using a model of single carrier SCL current with a field-dependent mobility.

of $J_{sc}=105$ A/m², $V_{oc}=0.59$ V, and $FF=60\%$ have been obtained. The strong increase of J_{sc} and the relatively small loss in FF lead to an enhanced efficiency of 3.7%. The efficiency increase found here is similar to the one reported by Li *et al.* when measured under standard AM1.5 conditions.¹⁵ In Fig. 2 the SCL hole-only currents are shown for the fast ($L=220$ nm) and slowly dried ($L=408$ nm) films. For the fast dried and annealed film the current density (J) vs voltage (V) characteristics are quadratic, as expected for a SCL current. The solid line is the calculated current employing a hole mobility $\mu_h=1.1\times 10^{-8}$ m² V⁻¹ s⁻¹, similar to the value reported before.¹⁴ For the slowly dried films a mobility of $\mu_h=5.0\times 10^{-7}$ m² V⁻¹ s⁻¹ is obtained, accompanied by a negative field dependence. Such a negative field dependence has been observed for pristine P3HT (Ref. 17) as well as P3HT:PCBM blends,¹⁸ and it is attributed to large spatial disorder of the charge transport sites. Applying slow drying we observe that the hole mobility in the P3HT phase increases by a factor of 45 with respect to the annealed films of Fig. 2, and compared to a previously reported value for annealed films it is 33 times higher.¹⁴ Furthermore, the measured mobility is almost two orders of magnitude larger than the earlier reported values for slowly dried films.¹⁵

In order to study the effect of such a mobility increase on the efficiency we apply a recently developed numerical device model⁵ to analyze the photocurrent J_L of the solar cells, as represented in Fig. 1. In this model the photocurrent in conjugated polymer/fullerene blends is dominated by the dissociation probability $[P(E,T)]$ of electron-hole pairs at the donor/acceptor (D/A) interface, which is a field- and temperature-dependent process.^{6,19} The input parameters required to calculate the photocurrent in the model are μ_e and μ_h , the spatially averaged dielectric constant $\langle\epsilon_r\rangle$ of P3HT and PCBM, the dissociation parameters a and k_F^{-1} , and maximum generation rate G_{max} . G_{max} was determined from the full saturation of the photocurrent, and a and k_F^{-1} were determined from the field-dependent dissociation probability $P(E,T)$ by fitting the temperature dependence of the photocurrent. Using $\mu_h=1.1\times 10^{-8}$ m² V⁻¹ s⁻¹ and $\mu_e=3.0\times 10^{-7}$ m² V⁻¹ s⁻¹, $a=1.8$ nm and $k_F^{-1}=7\times 10^{-5}$ s, and $G_{max}=6\times 10^{27}$ m⁻³ s⁻¹ the photocurrent of the annealed device is consistently described, as shown in Fig. 3. For comparison, we also calculated the photocurrent for a device with a thickness $L=304$ nm, keeping all other parameters fixed. It

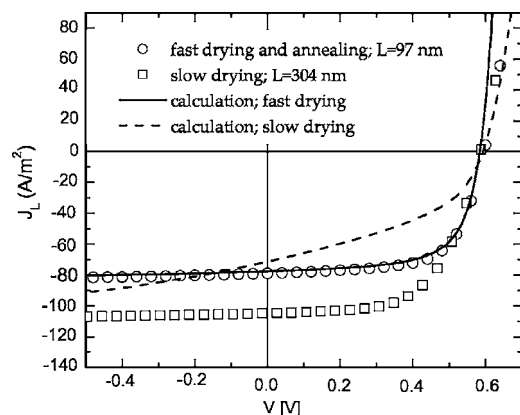


FIG. 3. Experimental photocurrent-voltage characteristics (J_L - V) of the devices presented in Fig. 1 together with the model calculation (solid line) using the measured hole and the electron mobilities for the fast drying film. The remaining model parameters are identical to the ones determined in a previous study (Ref. 14). As a comparison, also the photocurrent for a 304 nm device is calculated (dashed line) using the model parameters of the quickly dried and annealed device.

is evident from the curve that the fill factor strongly reduces to a value of only 42%, which is detrimental for the performance. Such a low fill factor is indicative for the formation of space charge in such a thick active layer device.⁹ In this case, an increase of the active layer thickness L will lead to an increase of the photocurrent until it reaches the thickness independent space-charge limit. Then, a transition will occur from a non-SCL to a SCL device, leading to a strong decrease of the fill factor.²⁰ As a result, for a thick 304 nm device already a mobility difference of one order of magnitude is sufficient to induce significant space-charge effects.

In Fig. 4 the photocurrent of the slowly dried device is modeled using the enhanced mobility of $\mu_h = 5.0 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ as input, while the other parameters were kept the same, except for G_{max} that was fitted from the photocurrent under reverse bias. Taking the enhanced mobility into account, the calculated photocurrent is in excellent agreement with the measurements. As a reference the dashed line of Fig. 3, using the lower mobility, is also included in the plot. As expected, the increase of the mobility leads to a strong enhancement of the FF, going from 42% to 61%. The small loss compared to the thin device shown in Fig. 3 (FF = 66%) is overruled by a significant increase of the J_{sc} due to the increased absorption, enhancing the power efficiency from 3.1% to 3.7%. The role of the increased mobility is that the transition from non-SCL towards the SCL regime is extended to higher thickness. With a mobility of $\mu_h = 5.0 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, the 304 nm device is still in the regime where space-charge effects do not play a role. This is also confirmed by the linear intensity dependence of J_{sc} . We also note that with the low mobilities reported before¹⁵ it is not possible to obtain a good fit of the experimental data. With these low mobilities, the calculated recombination losses in the device strongly increase, thereby lowering the FF far below the experimental values.

In conclusion, the origin of the enhanced performance in P3HT:PCBM bulk heterojunction solar cells, made with slowly dried active layer films, was investigated. Using hole transport measurements, we demonstrate that slow drying leads to a 33-fold enhancement of the hole mobility, reaching a value as large as $5.0 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the P3HT phase

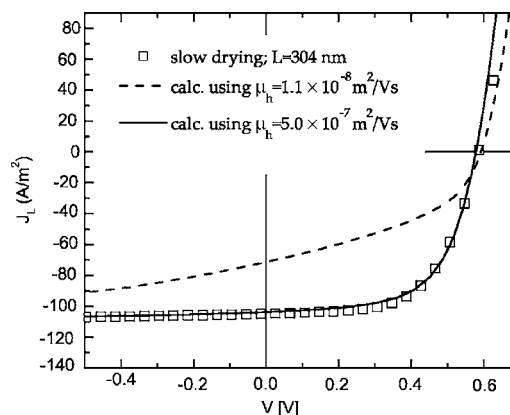


FIG. 4. Experimental photocurrent (J_L) of a P3HT:PCBM blend solar cell device, prepared by the slow drying method of the photoactive layer (squares), together with the model calculation, using a hole mobility measured in the fast drying film (dashed line) and slow drying film (solid line).

of the blend. This mobility increase reduces the accumulation of space charges in films with the necessary thickness to absorb most of the incoming photons. The resulting increase in short-circuit current together with the preserved fill factor increases the power conversion efficiency of these cells to a value of 3.7%.

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